

CHEMICAL DEFENSE AND MAMMALIAN HERBIVORES

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Summary

Herbivory is the interplay of plant form and function, herbivore anatomy and physiology, and foraging behavior. At the center of this interaction are the products of plant metabolism. Plants are producers of chemicals that can be classified as either primary or secondary metabolites. Primary metabolites are responsible for plant growth and also provide the nutrients mammals seek. Secondary metabolites are plant chemicals that, in part, defend plants against herbivores (toxins and antifeedants), pathogens (phytoalexins), and competing plants (allelochemicals). Chemical defenses deter mammalian herbivores by adversely influencing the physiology of the consumer. Defensive compounds vary not only among plant species, but also in space and time within individual plants. Herbivores

may also influence how secondary metabolites are distributed in plants.

At the same time, herbivores have evolved both physiological and behavioral traits to circumvent plant defenses. Physiologically, herbivores are equipped with metabolic pathways designed to detoxify and eliminate defensive compounds. Behaviorally, herbivores “spread the risk” of consuming a toxic diet by eating a variety of foods (generalists) or focus their foraging efforts on a single plant species (specialists). Food mixing may also nutritionally guarantee that the herbivore can detoxify defensive compounds. However, neither the herbivores nor the plants have gained the advantage in this evolutionary arms race. Rather, evolutionary feedbacks have prevented both plants and herbivores from gaining the upper hand.

Plant chemicals (phytochemicals) contribute to the flavor of a plant as well as impact the well-being of the herbivores that ingest them. Both primary and secondary metabolites must be considered when assessing herbivory. Mammalian herbivores learn about the foods they eat from the interplay of phytochemicals and the physiological effects they produce. Learning produces aversions and preferences for other attributes of the food (what a food smells, looks, or feels like; where it may be found; who else eats it).

Both chemical defense allocation by plants and herbivory by mammals are dynamic, adaptive processes. Plants are capable of adapting to changing environmental conditions and herbivory. Herbivores are similarly equipped to recognize phytochemicals in the foods they eat and respond accordingly. These responses, both physiological and behavioral, permit mammalian herbivores to forage efficiently in the diverse and ever-changing phytochemical world they inhabit.

1. Plant Metabolism

1.1. Primary Metabolism

The universal constituents of plant cells and tissues are known as primary plant metabolites. They are the primary products of plant growth and the targets of foraging mammals. Examples include simple carbohydrates (e.g. glucose, sucrose), starches (e.g. amylose, amylopectin), lipids (e.g. triacylglycerol), and proteins (e.g. globulins). Carbohydrates are the principle products of photosynthesis. Most of the carbon dioxide fixed by plants is initially transformed into sucrose, the main storage sugar in plants. Sucrose can be easily broken-down into its component sugars via enzymatic hydrolysis. The plant enzyme invertase converts one molecule of sucrose into a molecule of glucose and a molecule of fructose. Cellulose (a polymer comprised of repeating glucose molecules) is the most abundant plant polysaccharide, providing the framework of plant cell walls.

Starch, a mixture of amylose (a linear molecule of 600 - 3,000 glucose units) and amylopectin (a branched molecule of 6,000 - 60,000 glucose units) is the pre-eminent source of stored carbohydrates in plants. A variety of starch-degrading enzymes are available in plants to produce any number of smaller oligosaccharides, maltose, and glucose directly from starch.

Lipids serve many functions in plants, including formation of cell membranes and exterior cuticle surfaces of aerial tissues. Triacylglycerol, three long-chain fatty acids attached to a glycerol molecule, is a prime form of carbon storage in seeds and a major source of calories for herbivores. Lipids may be enzymatically oxidized to yield free fatty acids for energy and sugar production.

Proteins are a source of nitrogen storage and account for a substantial portion of the dry weight of plants. Proteins and peptides are composed of amino acid building blocks, which lead to the great diversity in protein size and function. The numerous plant enzymes responsible for biochemical functions such as synthesis and metabolism of starch and lipids are also proteins.

1.2 Secondary Metabolism

Secondary plant metabolites differ from primary metabolites in that they do not contribute directly to plant growth and are not distributed universally in plant tissues. These metabolites take on many roles in plants, including serving as visual and olfactory cues for pollinators and seed dispersers. However, the most prominent role of secondary metabolites is defending plant tissues against herbivores, pathogens, and competing plants. The types and amounts of chemical defenses are often regulated by the plant and may be predicted. Chemical defenses against mammalian herbivores can be classified as either toxins or antifeedants. Toxins are normally present in relatively low concentrations in plants and extremely poisonous. Conversely, antifeedants are typically present in large quantities and not highly toxic to herbivores.

Monoterpenes and phenolics are the most common antifeedants in plants. Numerous vascular plants employ monoterpenes and phenolics to minimize mammalian herbivory on above-ground structures. Monoterpenes are the simplest volatile terpenes found in conifers, mints, composites, and citrus. They serve as toxins, oviposition stimulants, and feeding deterrents for insects. However, mammalian avoidance of many plants has also been linked to the antifeedant qualities of monoterpenes. Monoterpenes can be toxic in high doses, though mammals have sophisticated mechanisms to detoxify them. In toxic doses, monoterpenes inhibit acetylcholinesterase activity in mammals. In conifers, monoterpenes are present in high concentrations in the foliage and the vascular tissues.

Phenolics are a broad category of secondary metabolites that include tannins, lignins, and flavonoids. Tannins are found in the sap of living cells, in plant resins, and in plant and are classified as condensed or hydrolyzable. Condensed tannins are complex molecules consisting of repeating units of smaller phenols. Condensed tannins are not easily reduced into the smaller building blocks. Conversely, hydrolyzable tannins are readily broken down to the basic structural unit via acid, base, or enzymatic hydrolysis.

Tannins deter herbivores by inhibiting digestion and may also be toxic in large quantities. Mammalian plant avoidance has been correlated with tannin content for numerous plant species. Digestibility is inhibited when tannins form complexes with soluble plant proteins and carbohydrates as well as with mammalian digestive enzymes. Tannins are also known to impart astringency when ingested, however it is probable that astringency per se does not

deter feeding. Rather, mammals may rely on learning processes to associate the sensation of astringency with inhibited digestibility.

Lignins are polymeric phenolics of high molecular weight that contribute rigidity to cell walls and internal structures of erect plants. Lignins deter herbivory via increased toughness of plant tissues and decreased digestibility (i.e. a physical defensive mechanism). Thorns, spikes, and hairs (trichomes) are examples of other physical defenses of plants. These structures can discourage sampling and decrease intake rates of plant tissues by both vertebrate and invertebrate herbivores. In general, physical defenses are most common in dry ecosystems and in regions of high herbivore densities.

Flavonoids, another class of phenolics, are important pigments contributing to flower, fruit, and leaf color. While most flavonoids are considered non-toxic, some such as rotenone are highly toxic. Flavonoids are just one of many plant toxins that in small concentrations may deter herbivory. Other toxins include cardenolides (present in milkweeds), glucosinolates (mustards), furanocoumarins (parsnip), cyanogenic glycosides (legumes, sorghum), saponins (snakeweeds), and alkaloids (numerous herbaceous and woody plants).

Like alkaloids or cardenolides, many sesquiterpenes (the largest class of terpenoids) are also extremely poisonous and would be considered toxins rather than antifeedants. Sesquiterpenes are extensively variable in chemical structure and toxic to both insects and mammals. Herbaceous plants such as bitterweeds (*Hymenoxys spp*) and sneezeweeds (*Helenium spp*) contain sesquiterpene lactones that bind to sulfur-containing essential amino acids. As compared to monoterpene antifeedants, sesquiterpene lactones are toxic in much smaller doses. For example, the oral dose of α -pinene (a monoterpene common in conifers) required to produce mortality in fifty percent of rats tested (LD50) is 3700 mg/Kg, whereas the LD50 for helenalin (a sesquiterpene lactone found in sneezeweed) is 150 mg/Kg.

The metabolic effects of these toxins vary among herbivores. The plant itself is the first source of variation. The concentration of toxins may vary from tissue to tissue and over time. Among mammals, detoxification processes allow herbivores to tolerate certain levels of these phytochemicals. The herbivore's ability to tolerate specific toxins is determined by dose, mode of action, metabolism, and nutritional state.

2. Phytochemical Variation in Plants

2.1 Variation within a Population

Just as plant morphology differs among plant species, so too do phytochemical constituents. The heritability of phytochemicals has been extensively studied in many plants, particularly monoterpenes in conifers. The pattern of terpene allocation in conifers may be controlled by only a few genes. Importantly, preferences of mammalian herbivores for certain plant genotypes and hybrids have been attributed to heritable defensive chemicals. In general, genetics dictate which phytochemicals are present while environment influences their relative abundances. However, patterns of defense allocation in response to the environment are scattered and difficult to predict. For example, mineral

and water stress in conifers causes the concentrations of some monoterpenes to increase, while others decrease or are unaffected.

Biotic pressures also exert themselves on the expression of phytochemicals present in plants. The adaptive response of one species in response to the genetic changes of another is termed coevolution. Diffuse coevolution describes a system in which groups of populations evolve in response to genetic changes in each other. In order to affect a response, a population must exert a strong selective pressure. Because mammals are typically generalist herbivores, they probably have not played much of a role in coevolution of plant defenses. Interactions between plants and a variety of competitors, pathogens, abiotic factors, and insect herbivores likely have led to much of the phytochemical diversity observed today. However, mammals must deal with the suite of defenses arising in plants, regardless of the driving force.

2.2 Variation within an Organism

In addition to variation among species, the types and abundances of phytochemicals also vary within an individual plant. Because different plant tissues perform different functions, it is expected that secondary metabolites would vary among plant parts. For example, phytochemicals present in reproductive tissues that attract pollinators would not be necessary in the roots. The transportation systems of vascular plants allow phytochemicals to be translocated to specific organs. Concentration gradients have often been observed for many phytochemicals. For example, many plants exhibit great variation in terpene concentration among leaves, roots, stems, and reproductive parts.

Phytochemicals also vary temporally within plants. Seasonal changes in foliage phytochemistry are common. Maturation of Douglas-fir foliage includes increased concentrations of many terpene compounds. This trend of higher terpene concentration in older tissues is common in other organs such as stems and roots. Though temporal variation is usually considered in the context of seasonal or maturation effects, it is not limited to large-scale variation. Phytochemical variation can occur on an hourly scale. For example, diurnal variability of plant carbohydrates occurs because the rate of photosynthate export does not equal the rate of photosynthesis over the entire photoperiod. Such variation is significant and can be detected by foraging herbivores.

Direct changes in the distribution or abundance of plant defenses resulting from herbivory or environmental stress are termed induced responses. Induction allows plants to produce costly defenses only when they are needed. For example, mammalian herbivory can cause plants to increase the abundance of chemical defenses in new growth.

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Biographical Sketches

Bruce Kimball is a research chemist with the USDA National Wildlife Research Center (NWRC). The mission of the NWRC is to develop new tools to solve wildlife-human conflicts. Bruce received his M.S. (Analytical Chemistry) from Arizona State University and his Ph.D. (Ecology) from Colorado State University. His primary research focuses on chemically mediated behaviors in mammalian wildlife. This includes investigating chemical constituents present in natural systems and examining relationships between phytochemistry and wildlife use of agricultural resources. His research is conducted in the field, with captive animals, and in the chemistry laboratory.

Fred Provenza's research focuses on understanding behavioral principles and processes and using that understanding to inform management. For the past two decades, his research team has studied the role of learning in food and habitat selection by herbivores. He has co-authored 115 papers in peer-reviewed journals and his group has been asked to co-author an additional 51 synthesis papers for peer-reviewed journals, books, and proceedings. In 1999, he received the W.R. Chapline Research Award from The Society for Range Management for exceptional research accomplishments that enhance management of landscapes. This award is given annually to the person whose research most embodies excellence in Range Science. In 1999, he also received the University Outstanding Graduate Mentor award from Utah State University. He has supervised

45 graduate - M.S. and Ph.D. students – and post-doctoral students from 19 different countries.

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